

# Optical Properties and Correlation Effects in $\text{Na}_x\text{CoO}_2$

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We have calculated the optical spectra of  $\text{Na}_x\text{CoO}_2$  for  $x=0.3, 0.5$ , and  $0.7$  within the LDA. We compare our results to available experimental data and show that the important features and trends are reproduced well, but there is a nearly uniform shift of peak positions and poor agreement in intensities. We show, through application of a simple model, that these differences can be attributed to overhybridization between Co and O orbitals and spin fluctuations which renormalize the bandwidth. Applying the LDA+U procedure shifts the optical peaks further from their experimental locations, indicating that this method of incorporating correlation effects is ill-suited for the case  $\text{Na}_x\text{CoO}_2$ .

The layered cobaltate  $\text{Na}_x\text{CoO}_2$  is the subject of considerable interest not only because of a possibly unconventional superconducting state<sup>1</sup>, but also an unusual phase diagram that encompasses two very different metallic states, and at least one insulating region<sup>2</sup>, and unusual magnetotransport and thermoelectric behavior.<sup>3,4,5</sup> For  $x < 0.5$ , the system behaves as a paramagnetic metal with Pauli-like susceptibility and superconducts when hydrated in the narrow region around  $x=0.3$ . At  $x=0.5$ , a charge ordered insulating state, which is likely anti-ferromagnetic, occurs. When  $x$  is increased above  $0.5$ , the metallicity returns, but the susceptibility becomes Curie-Weiss like,<sup>6</sup> and a spin-density wave appears<sup>7</sup> around  $x=0.75$ . It has been recently reported<sup>8</sup> that, at low temperatures, a second insulating state may set in at  $x=0.25$ .

LDA calculations show<sup>9</sup> a band structure that evolves smoothly with  $x$ , in contrast to the sharply different regions described above. The experimental phase diagram is not well reproduced, and a weakly ferromagnetic, metallic ground state is found incorrectly for all Na concentrations. Neglect of strong correlation effects by the LDA is the most obvious culprit, but their precise role in  $\text{Na}_x\text{CoO}_2$  is not understood. Circumstantial evidence indicates that it is substantial, with most estimates of the Hubbard  $U$  quite large in comparison with the  $t_{2g}$  bandwidth. However, the system does not behave characteristically as a doped Mott-Hubbard insulator, particularly around the superconducting composition where susceptibility measurements indicate a lack of local magnetic moments on Co  $d$  ions.<sup>10,11</sup> Also important is the observation that LDA calculations in systems with strong Hubbard correlations routinely underestimate the tendency to magnetism (the larger the difference,  $U - I$ , between the Hubbard repulsion and Hund rule coupling, the greater the underestimation)<sup>12</sup>, and overestimate the antiferromagnetic superexchange  $J$ . In the LDA,  $\text{Na}_x\text{CoO}_2$  is magnetic<sup>13</sup>, with antiferromagnetic instabilities that are smaller than ferromagnetic. This requires effects beyond LDA to suppress magnetism and casts doubt on frustration as a mechanism for suppression of magnetism. Because of this, despite the large  $U/W$  ratio, spin fluctuations may offer a more plausible reason for the deviations from the LDA.

In this context, it is important to verify to what extent LDA bands correctly describe the one-electron excitations and fermiology of  $\text{Na}_x\text{CoO}_2$ . Quantum oscillation probes would be ideal to investigate the Fermi surface (FS), particularly the predicted small pockets<sup>13,14</sup>, but so far no such studies have been reported. Several photoemission reports are available<sup>15,16</sup>, but because the electronic structure is expected to be sensitive to both surface states and surface quality, generalization of these results to the details of bulk electronic properties is questionable. Infrared optics has a penetration depth of  $\sim c/\omega_p$  (where  $\omega_{pl}$  is the plasma frequency), much longer than that of photoemission ( $\sim 10 \text{ \AA}$ ), and may therefore provide the most reliable probe of the electronic structure available to date. Several of these experiments have been reported<sup>8,17,18,19,20</sup>. However, since optical absorption is an integrated property, involving a variety of interband transitions, it is usually difficult, if even possible, to interpret the results in terms of the electronic structure without full first principles calculations.

Here we report such calculations. By comparing our calculated LDA spectra with optical experiments reported for various Na contents, we are able to assign the three main peaks to specific interband transitions and thereby examine in detail the dependence of these peak positions and strengths on bandwidths and energies. The peak shifts one expects to see in Mott-Hubbard type compounds are not realized in this system, even for the insulating compounds. Furthermore, application of the LDA+U methodology exaggerates the systematic discrepancies between the LDA and measured spectra. We employ a simple model to illustrate that overestimation of Co-O hybridization due to overly extended d-orbitals would produce precisely the kind of peak shifts we see in our LDA spectra. Spin fluctuations predicted early on<sup>21</sup> and later observed<sup>22</sup> at some values of  $x$ , could also affect the spectra by renormalizing the bandwidth of the  $t_{2g}$  complex. This is also consistent with the differences we observe in our transitions compared with experiment.

## I. CALCULATED OPTICAL CONDUCTIVITY

Using the Wien2k<sup>23</sup> full-potential augmented plane wave + local orbital code (APW+lo), we calculated the optical conductivity for  $\text{Na}_x\text{CoO}_2$  at three Na contents:  $x=0.3, 0.5$  and  $0.7$ . To vary the Na content, we used the virtual crystal procedure of occupying each site with an ion of fractional charge. For both  $c$  and  $a$  lattice constants, we used experimental data<sup>2</sup> but relaxed the apical O height separately at each  $x$ . The APW sphere radii were the same for all calculations: 2.0 for Na, 1.85 for Co and 1.55 for O.  $Rk_{\text{max}}$  (essentially a measure of the plane-wave cut-off) was set to 7.0, giving a basis set of 833 APW's and 60 local orbitals. Our density was well converged using 480  $k$ -points in the irreducible Brillouin zone (BZ).

We first calculated the imaginary part of the dielectric constant,  $\epsilon''(\omega)$  in the random phase approximation (RPA) using the standard code of the Wien2k package. The real part of the optical conductivity,  $\sigma'(\omega)$ , can then be obtained by  $\sigma'(\omega) = \frac{\omega}{4\pi} \epsilon''(\omega)$ . The resulting spectra exhibit three main peaks, which we label  $\gamma$ ,  $\beta$ , and  $\alpha$ , according to the notation of Wang *et al*<sup>19</sup>. We can identify the specific interband transitions giving rise to these peaks using a band by band decomposition of  $\epsilon''(\omega)$ . Each of  $\gamma$ ,  $\beta$ , and  $\alpha$  have distinct origins. The  $\gamma$ -peak corresponds to transitions between different bands of the metallic  $t_{2g}$  complex, the  $\beta$ -peak to  $t_{2g}$ - $e_g$  transitions, and the  $\alpha$ -peak to transitions from fully occupied O- $p$  states to unoccupied  $e_g$  states. Note that the  $\gamma$  and  $\beta$  peaks exist despite the dipole selection rule which forbids  $d$ - $d$  transitions, because of O hybridization throughout both  $d$ -band complexes. The  $t_{2g}$  bands are split into an  $a_{1g}$  and two  $e'_g$  bands by the trigonal crystal field<sup>13</sup>, and all  $\gamma$  transitions are from a lower  $e'_g$ -like state to an upper  $e'_g$  or  $a_{1g}$ -like state. The  $e'_g$ - $e'_g$  transitions are wholly due to small hole FS's near the  $K$  points of the BZ and contribute to the lowest visible peak in the calculated spectrum (the  $\gamma$  subpeak near 0.4 eV in Fig. 1). However, there are allowed  $e'_g$ - $a_{1g}$  transitions in the same energy range that contribute roughly equally to the peak intensity and therefore, the existence of these hole pockets cannot be inferred from the existence of the peak. The calculated  $\beta$  peak has several distinguishable subpeaks corresponding to transitions from different parts of the BZ. In Fig 1, the peaks of the spectrum for  $\text{Na}_{0.5}\text{CoO}_2$  are shown and representative transitions are indicated along high symmetry points of the corresponding band structure.

## II. COMPARISON WITH EXPERIMENT

The three ( $\gamma$ ,  $\beta$ ,  $\alpha$ ) conductivity peaks are clearly recognizable in all available optical data. The reported positions and strengths of these peaks, however, vary somewhat between experiments, even for identical dopings<sup>8,18,19</sup>. For consistency of comparison, we use

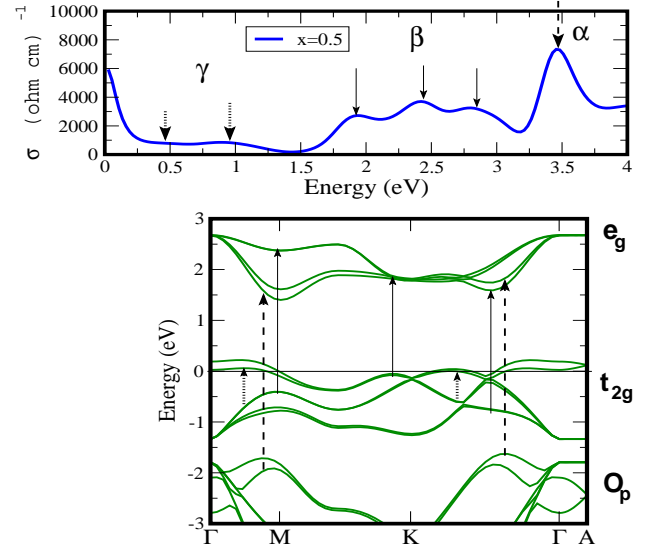


FIG. 1: *top panel* The LDA optical conductivity for  $\text{Na}_{0.5}\text{CoO}_2$  with arrows delineating the three main peaks:  $\gamma$  (lined arrows),  $\beta$  (solid arrows) and  $\alpha$  (dotted arrows) A Gaussian broadening of 0.06 eV was used. *bottom panel* Interband transitions corresponding to peaks in the optical conductivity.

mainly the report of Hwang *et al*<sup>8</sup>, where spectra for several compounds of different Na content are available. Overall, the LDA spectra are seen to be in good qualitative, but poor quantitative agreement with experiment (see Fig. 2), a situation we will attribute to LDA overhybridization, and/or spin fluctuations in the next section. But first, we discuss the doping dependencies and general shape of the spectra. These are well reproduced by calculation. There are two clear trends followed by both the LDA and measured  $\sigma_1(\omega)$  as electron count is increased (Na added). First, the  $\alpha$  and  $\beta$  peaks shift away from each other and become broader. Second, the  $\gamma$  peak sharpens and moves slightly lower in energy. Both effects have their origin in an upward shift of Co-derived bands as the Co  $d$  band filling is increased. The greater energy difference between the O- $p$  states and the shifted  $e_g$  band determines the  $\alpha$  peak position, and a reduction in hybridization between Co and O orbitals, now further separated in energy, weakens the  $t_{2g}$ - $e'_g$  crystal field splitting, causing the downward  $\beta$ -peak shift. Since the  $\gamma$ -peak is due to transitions within the  $t_{2g}$  band complex, its sharpening and shift down are both attributable to a slightly narrowed  $t_{2g}$  bandwidth caused by decreased O mixing. Our calculated in-plane plasma frequency at  $x=0.7$ ,  $\omega_p = 1.39$  eV, agrees well with values extracted from experiment<sup>18,19</sup>:  $\omega_p = 1.48$  eV and  $\omega_p = 1.17$  eV. The c-axis plasma frequency is calculated to be 1.48 eV, nearly the same as the in-plane value, reflecting the lack of anisotropy at higher Na levels<sup>24</sup>. As Na is removed, the in-plane plasma frequency and the electronic anisotropy increase until, at  $x=3$ , the in-plane  $\omega_p$  is 2.86 eV and the c-axis  $\omega_p$  is 0.337 eV, approximately an order of magni-

tude apart. The increase in Drude weight and concurrent enhancement of anisotropy with electron removal are in good agreement with experimental observations<sup>8,17</sup>.

Despite these instances of good agreement, some dramatic differences between the spectra are obvious. The experimental peak intensities are almost a factor of two smaller and approximately 0.5 eV lower in energy than our calculated ones when a Gaussian broadening of 0.06 eV (this value reproduces all three reported peak widths well) is used. Experimentally, the strong dip just below the  $\alpha$  peak deepens from  $x=0.25$  to  $x=0.5$ , but then becomes shallow again at  $x=0.7$ , whereas the LDA gap deepens and widens monotonically with increasing Na content. It has been previously suggested both  $\beta$  and  $\alpha$  peaks could be identified with transitions across  $t_{2g}$ - $e_g$  energy gap and that spin splitting of  $t_{2g}$  states could account for differences between observed peak positions and calculated paramagnetic band positions<sup>19</sup>. Though no observation of static magnetism has been made for any  $x < 0.75$ , the LDA is known to predict an FM ground state for all  $x$ , suggesting that magnetic fluctuations may be present in the system<sup>13,21</sup>. Direct observations of FM spin fluctuations<sup>22</sup> and a spin density wave<sup>7</sup> at  $x=0.75$ , and c-axis AFM ordering<sup>25</sup> at  $x=0.85$  further support the idea that magnetism may play a role in optics. However, since regular optics does not allow for spin-flip transition, spin splitting may shift optical transitions only if one of the two electronic states involved in a transition is split and the other is not. This is not the case for either  $\gamma$  or  $\beta$  peaks. There is some effect on the position of the  $\alpha$  peak, because of oxygen admixture, but it is merely 0.15 eV even at  $x=0.3$ . Thus, the observed shifts of the absorption peaks compared to LDA, especially the two high-energy peaks,  $\alpha$  and  $\beta$ , cannot be due to magnetic effects.

### III. CORRELATIONS EFFECTS AND BAND RENORMALIZATIONS

The small  $t_{2g}$  and  $e_g$  bandwidths of  $\text{Na}_x\text{CoO}_2$  suggest that correlation effects in Co-d may be important. Our renormalized atom calculations for Hubbard  $U$  on Co yield  $U \gtrsim 3.7$  eV, while the  $t_{2g}$  bandwidth  $W$  is 1.5 eV, so that the Hubbard ratio (accounting for degeneracy) is  $U/W\sqrt{3} \gtrsim 1.5$ . Spin-unrestricted band structure calculations yield a half-metallic ferromagnetic ground state, contrary to experiment. All this suggests that conventional LDA calculations should be taken with a grain of salt in this compound, and it is quite likely that the actual experimental electronic structure is considerably renormalized compared to the LDA results. Indeed, angle-resolved photoemission spectroscopy (ARPES) measurements<sup>15,16</sup> have detected a heavy quasiparticle band near the Fermi energy with a total width of  $\sim 70$  meV, much smaller than the LDA bandwidth. This is an interesting finding, but surface sensitivity should be kept in mind. Indeed, differences between

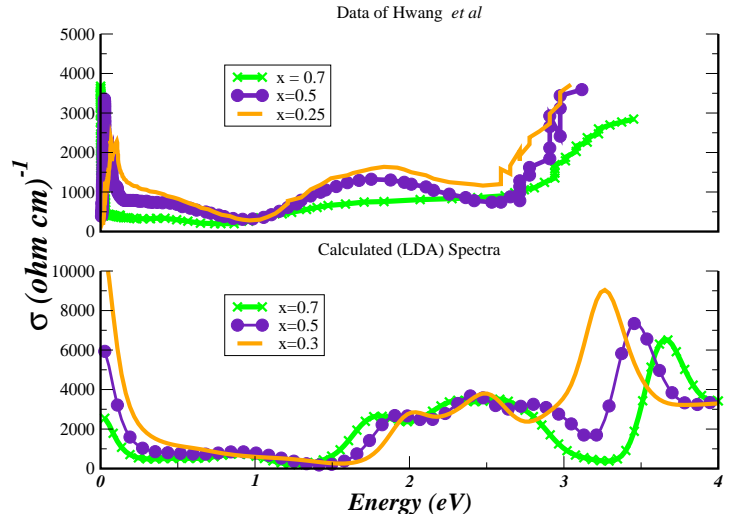


FIG. 2: (color online) A comparison of experimental (top panel) and calculated (lower panel) optical spectra. Note that the lowest calculated Na concentration is 0.3, slightly different from the experimental value of 0.25.

surface electronic structure, as measured accurately by ARPES, and bulk electronic structure have been established in other oxides, including cuprate<sup>26</sup>, ruthenate<sup>27</sup>, and manganite<sup>28,29</sup> compounds. Optical experiments, with their longer penetration depth have the potential to tell us more about the specific shortcomings of LDA calculations in sodium cobaltate.

Let us first recall the typical inadequacies of LDA calculations in systems with localized electrons. The best known case is exemplified by Mott-Hubbard insulators. Here the missing physics is mainly the Coulomb repulsion between electrons localized at the same site. Typical examples are  $f$ -electron compounds, high- $T_c$  cuprates, or  $3d$  oxides. This group is characterized by (1) underestimation of propensity toward magnetism (up to the level of total loss of a magnetic ground state, as in cuprates) (2) underestimation of band gaps between occupied and empty bands and (3) overestimation of the superexchange antiferromagnetic interaction (this increases with hopping and decreases with the band gap; the former is overestimated and the latter underestimated in LDA). As a leading correction to the LDA, the LDA+ $U$  method has been very successful in the prototypical systems listed above. For these, the LDA+ $U$  method reproduces the missing Mott-Hubbard effects, such as “sinking” of the occupied bands relative to the unoccupied bands (with corresponding shifts of interband transitions to higher energies).

Inspection of the LDA bandstructure of  $\text{Na}_x\text{CoO}_2$  in conjunction with experimental data indicates that this physics is not applicable here. The tendency toward mag-

netism is *overestimated*, and so is the band gap between the  $t_{2g}$  and  $e_g$  bands. The LDA ground state is ferromagnetic, and not antiferromagnetic. Not surprisingly, LDA+U calculations<sup>30,31</sup> only worsen the situation. The  $t_{2g} - e_g$  distance, already 0.5 eV too large, increases further, and the tendency towards magnetism becomes even stronger. Additionally, for more subtle reasons, the two  $e'_g$  subbands of the  $t_{2g}$  manifold are shifted down with respect to the  $a_{1g}$  band. This in turn shifts the  $\gamma$  peak, already too high in energy, up even further. We conclude that the *LDA+U approach is not appropriate for  $\text{Na}_x\text{CoO}_2$* .

Another possible manifestation of electron-electron correlations we is found in  $^3\text{He}$  and in  $\text{CrO}_2$ <sup>32</sup>. Here collective excitations (magnons or paramagnons) play the same role as phonons in the sense of “dressing” quasiparticles and increasing their mass<sup>33</sup>. As a result, the optical spectra more or less proportionally squeeze toward the low frequency. Softening of magnetic excitations near a quantum critical point leads to large spin fluctuations and suppression (full or partial) of magnetic ordering<sup>34,35</sup>. A comparison of the experimental and calculated properties of  $\text{Na}_x\text{CoO}_2$  indicates the presence of such effects. Thus, *quantum criticality is likely to be an important reason for deviation from the LDA in  $\text{Na}_x\text{CoO}_2$* .

Finally, one should not forget about a very prosaic shortcoming of LDA: the fact that it includes a spurious self-interaction which leads to overextended  $3d$  orbitals, and thus overestimated hybridization with ligand orbitals. This effect becomes stronger for more localized  $d$ -orbitals. For the narrow  $d$ -bands of  $\text{Na}_x\text{CoO}_2$ , this will be operative to some extent.

We shall now try to assess qualitatively the ramification of these two effects. The first, “dressing” of one-electron excitations is qualitatively similar to the electron-phonon coupling induced renormalization, except it occurs in a larger energy range. It is reasonable to expect it to affect the whole  $t_{2g}$  band or a large part of it, leading to overall narrowing of all three  $t_{2g}$  bands. This, in turn should shift both components of the  $\gamma$  transition, the  $e'_g - e'_g$  one and the  $e'_g - a_{1g}$  one to lower energies, without much change in their intensity (the extra spectral weight is transferred to high energies, as in the electron-phonon coupling). It is unlikely that, as sometimes assumed, the top of the  $e'_g$  band will be shifted down with respect to the  $a_{1g}$  band. First, dressing of the quasiparticles makes them heavier, but normally does not shift different states near the Fermi energy with respect to each other. Second, this would not only eliminate the  $e'_g - e'_g$  transitions, but would also shift the  $e'_g - a_{1g}$  to higher energy, opposite to what is required by the experiment. It is also unlikely that such “dressing” would affect the unoccupied  $e_g$  band, which is too far away from the Fermi level.

Let us now estimate the possible effects of contraction of the Co  $d$ -orbitals. To this end we use the simplest possible tight binding model, namely one where only nearest

neighbor Co-O  $pd\sigma$  and  $pd\pi$  hoppings (we will these  $t_\sigma^2$  and  $t_\pi^2$  respectively) are included, and the energy of the O  $p$  level is taken to be sufficiently far removed from the Co  $d$  level to be integrated out. Both assumptions are extremely crude, for direct Co-Co and especially O-O overlaps are not small, nor is the  $p - d$  energy separation small, but the model nonetheless provides a useful qualitative framework. The resulting  $5 \times 5$  Hamiltonian has a  $2 \times 2$   $e_g$  subblock with diagonal elements proportional to  $t_\sigma^2$ . Because there is no path connecting an  $e_g$  orbital on one site to any neighboring  $e_g$  orbital via oxygen, there is no dispersion in this subblock. The  $3 \times 3$   $t_{2g}$  subblock has noticeable dispersion controlled by  $t_\pi^2$ , with the overall upward shift of the same order. Finally there is a dispersive off-diagonal subblock, corresponding to O-assisted hopping between neighboring  $t_{2g}$  and  $e_g$  orbitals. The scale of this block is set by the product  $t_\sigma t_\pi$ . Note that in a cubic structure, such  $t_{2g}-e_g$  hopping through an intermediary O is impossible.

We now make a further simplifying assumption, that  $t_\sigma \gg t_\pi$ . We can then neglect the ligand field on the  $t_{2g}$  orbitals (proportional to  $t_\pi^2$ ), leaving only the ligand field on the  $e_g$  orbitals (proportional to  $t_\sigma^2$ ). Since the  $\beta$  peak is due to  $t_{2g} - e_g$  transitions, its position reflects a crystal field splitting of the Co  $d$ -states which results from a combination of electrostatic and ligand field effects. Using a linearized muffin-tin orbital (LMTO) calculation with the Co-O hybridization suppressed, we found that the crystal field splitting reduces from  $\approx 3.4$  eV to  $\approx 1$  eV. That is, the electrostatic crystal field is 1 eV, and the ligand field is 2.4 eV. The latter is probably overestimated because the LDA overhybridizes the Co  $d$  orbitals. Specifically, if  $t_\sigma$  were 12% smaller than its LDA value ( $\sqrt{2.4/1.9} = 1.12$ ), the  $\beta$  peak would shift down by 0.5 eV, in agreement with the experiment. Furthermore, the intensity of this peak would also be reduced, because the optical matrix elements in a two-band tight binding model scale with the off-diagonal elements of the Hamiltonian (this follows from the tight-binding definition of dipole matrix elements as  $\langle A_1 | \partial H / \partial \mathbf{k} | A_2 \rangle$ , where  $A$  are the eigenvectors), and these scale as  $t_\sigma t_\pi$ . This is in accord with overestimation of the  $\beta$  peak intensity and lends further support to our assumption that the LDA overestimates the  $pd\sigma$  hopping amplitudes in  $\text{Na}_x\text{CoO}_2$ , probably by some 10%.

#### IV. CONCLUSIONS.

We have calculated the LDA optical conductivity spectra of  $\text{Na}_x\text{CoO}_2$  and compared it with experimental data for several different Na contents. There is good qualitative agreement in terms of the number of peaks and their behavior with changing  $x$ , but exact peak heights and positions are not well-reproduced. Though the underlying reasons for this are likely correlation effects neglected by the LDA, we argue that using LDA+U as a remedy is inappropriate for this compound. Spin fluc-

tuation driven renormalization of the  $t_{2g}$  band complex and overextension of Co  $d$ -orbitals are shown to affect the optical spectrum in a manner consistent with the discrepancies between calculation and experiment. These cause narrowing of the  $t_{2g}$  band and reduction of crystal field splitting respectively, bringing LDA optical peaks into good agreement with experimental reports.

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